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MINERAL ACID PURIFICATION OPPORTUNITIES

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ABSTRACT

Extending the life of mineral acid baths is environmentally and economically attractive. There are technologies currently available that can offer these benefits. Two such technologies are diffusion dialysis and acid sorption. These two competing technologies were objectively evaluated using bench scale equipment to compare their ability to remove metal contaminants and recover free acid from a contaminated mineral acid bath.

This comparison provides some criteria for evaluation of each technology when applied to the recovery of hydrochloric acid (HCl) from iron (Fe) contaminated hydrochloric acid solutions. The solutions prepared in the laboratory for these tests closely approximate actual spent hydrochloric acid activation and cleaning baths.

While the results indicate that both technologies are effective in recovering free acid and removing iron from the test solutions, there are distinct differences between the two. The diffusion dialysis system achieved acid recoveries averaging 97% and iron rejection averaging 86%. Acid sorption achieved acid recovery and iron removal efficiencies of approximately 96% and 45%, respectively.

Conclusions for diffusion dialysis are:
- the diffusion dialysis system has a higher HCl recovery efficiency per gram of acid fed to it, but because of the degree of osmosis occurring within the membrane stack during these tests, the diffusate acid concentration is approximately 55 - 60% of the feed acid concentration,
- the diffusion dialysis system achieves greater percent rejection of the contaminant metal in the feed; approximately 52% higher than acid sorption in this case (osmosis acts to increase metal rejection)
- fresh make up acid will be required when processing a work tank with a diffusion dialysis system (quantity will be dependent on system performance and the ability to minimize osmosis),

Conclusions for acid sorption are:
- the acid sorption system has a lower HCl recovery efficiency per gram of acid fed to it, but because of how it was operated, the recovered acid product is actually more concentrated than the feed,
- the acid sorption system will eliminate the need for make up acid into the working tank (the recovered acid product will actually need diluted prior to re-introduction to the working tank),
- average metal removal efficiency range from the feed to product stream is 38 - 44%

These technologies may be operated in batch or continuous mode. Diffusion dialysis is more suited for continuous mode, due to the time required to reach equilibrium. Acid sorption has more flexibility to operate efficiently in either mode. Choosing a technology and mode of operation will be dependent on

purity requirements of the bath, the bath volume to be processed, and the required flow rate. Operating costs for each system will be minimal due to their simplicity. Equipment costs and product purity requirements will govern technology selection. These factors will vary from one application to another. Applications that require high bath purity and a low feed processing rate may be best suited for diffusion dialysis. Conversely, applications requiring higher feed processing rates, and less stringent bath purity may be more conducive to acid sorption. Correct technology selection must be based on the actual application and will vary based on the mineral acid and metal contaminant concentrations.

Overall, both technologies provide viable at-source opportunities for recovering acid and minimizing waste handling costs, while maintaining higher quality baths and increased productivity.

1.0 INTRODUCTION

Mineral acids are used in many applications throughout industry. Some of the more common applications include cleaning, activating, anodizing, and pickling of raw metal stock and finished metal parts. Mineral acids are also used for the same processes in repair facilities. For example, metal parts are processed in mineral acid baths after initial forming and manufacturing steps, after cleaning and prior to painting and plating operations. During use, the baths become contaminated with dissolved metal ions. Eventually, the concentrations of the dissolved metals reach a level that renders the bath depleted and no longer capable of performing properly. Present methods for maintaining acceptable metal contaminant levels consist of partial or complete bath dumps. This method of operation requires complete fresh acid bath make up and treatment or offsite disposal of the dumped solution. Due to their wide use, industry is recognizing the economic and environmental benefits of extending the life of mineral acid baths. There are technologies currently available that can offer these benefits. Two of these technologies are diffusion dialysis and acid sorption. These two competing technologies were evaluated to objectively compare their ability to remove metal contaminants and recover free acid from a contaminated mineral acid bath. Implementing such a technology offers the potential to minimize fresh acid bath make up costs and reduce treatment and/or offsite disposal costs. Maintaining consistently higher quality baths can also contribute to consistently higher quality product at lower costs.

2.0 DIFFUSION DIALYSIS THEORY

Diffusion Dialysis is a membrane separation technology that relies solely on concentration gradient between a dilute solution (deionized water) and a concentrated solution (contaminated acid) to effect transport of ions. The two solutions are physically separated by an anion permeable and ion selective membrane. The membrane acts as the barrier at which ion transport (migration) occurs. Ion migration across the membrane occurs due to the high concentration difference between the solute (acid) and the solvent (D.I. water). The anion permeable membrane allows negatively charged acid ions to migrate through the membrane, while rejecting the positively charged metal ions. In order to maintain electroneutrality, and because they are very small, positively charged hydrogen ions also migrate through the membrane.

A typical diffusion dialysis system is comprised of a stack of membranes with interior channeling to effectively increase surface area and promote ion migration. The membranes are usually formed from copolymers of polystyrene and divinylbenzene. Operation involves passing the feed acid stream into the bottom of the membrane stack and deionized water into the top of the stack. A countercurrent flow arrangement maintains the most effective concentration gradient throughout the entire membrane stack. Acid feed and deionized water head tanks are physically located above the membrane stack. This allows the head pressure from the height difference to push the fluid through the membrane stack. Flow control

devices such as metering pumps or control valves are typically placed on the lines exiting the stack. These flow control devices are used to optimize the flow rate of the exiting streams and improve the ion migration process. The two streams exiting the process are referred to as diffusate, the acid rich and metal depleted solution, and dialysate, the depleted acid and metal rich solution. Figure 1 schematically illustrates a typical diffusion dialysis system.
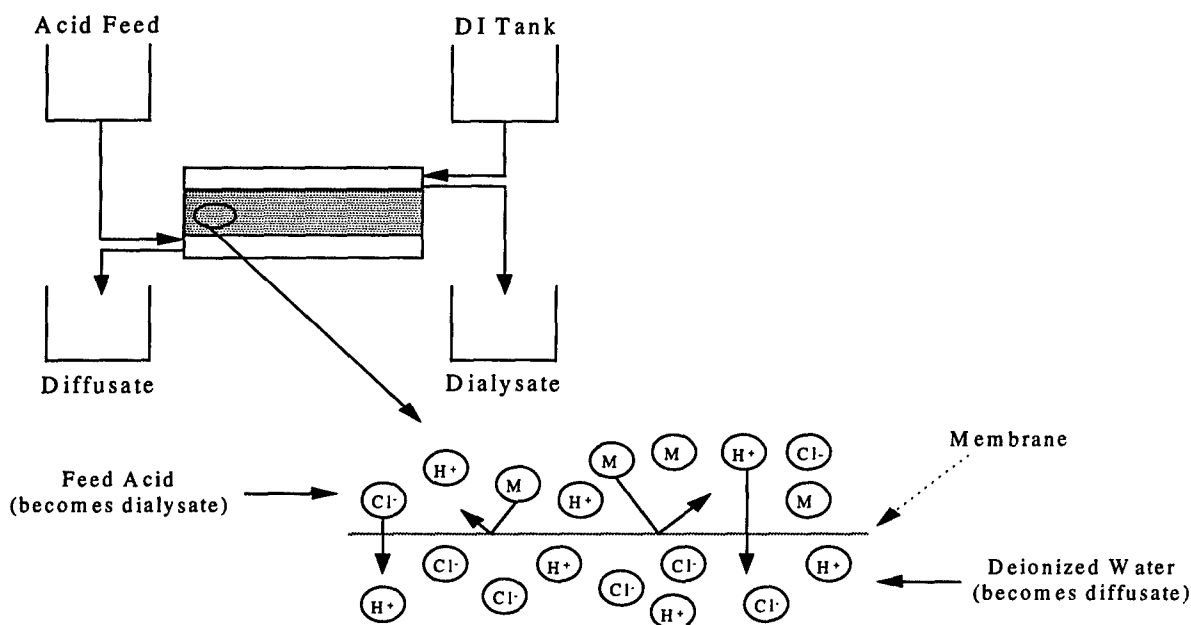

Figure 1. Diffusion Dialysis System

2.1 Process Considerations

Several physical variables affect the performance of a diffusion dialysis system. These variables are acid and metal concentrations, solution flow rates, and osmosis within the membrane stack.

Acid and metal concentrations in the feed acid greatly affect the efficiency of acid recovery and metal rejection. A feed solution with high acid concentration will typically give better percent acid recovery in the diffusate when compared to one with low acid concentration. This is due to the greater concentration gradient across the membrane. Conversely, a high concentration of metal in the feed acid tends to allow greater leakage of metal into the diffusate.

The flow rates of diffusate and dialysate must remain relatively constant. The ratio of flow rates between the two streams can range from 0.8 to 1.2. Varying the ratio of flow rates allows the operator to tailor the process to achieve different results. For example, operating the system with the diffusate flow rate higher than the dialysate flow rate will provide lower acid recovery and higher metal rejection. Operation with the diffusate flow rate lower than the dialysate flow rate will provide a higher acid recovery and lower metal rejection. This characteristic of the diffusion dialysis process allows flexibility to tailor the process to various applications.

Diffusion dialysis systems typically require 24 to 36 hours to reach equilibrium after initial start up. This is due to the relatively slow nature of the concentration gradient driven process and the corresponding long residence time requirement of the solution in the membrane stack. During the time required to reach

equilibrium the diffusate produced may not be acceptable for reuse. Periodic sampling (once every 8 to 12 hours during start-up) and analysis of the diffusate and dialysate is necessary to trend performance and note that equilibrium has been reached. Sampling and analysis frequency can be reduced once the process has reached equilibrium.

Actual operation of a diffusion dialysis system is relatively simple and does not require much operator intervention. Main requirements for proper operation are maintaining constant diffusate and dialysate flows and recording the volume of waste acid and deionized water fed to the system. It is very easy to study a diffusion dialysis system prior to observing one in operation and assume that the volume of feed acid fed to the system equals the volume of dialysate produced, or that the deionized water volume fed to the system equals the volume of diffusate produced. This, in fact, is not the case. The reason for this discrepancy is osmosis within the membrane stack. Just as the concentration gradient causes acid to migrate through the membrane into the deionized water, the same gradient causes osmosis, or water migrating through the membrane into the acid. The effect of osmosis, in this case, is that the feed acid stream becomes diluted. The effect of osmosis can be minimized by adjustment of the diffusate and dialysate flow rates. However, in addition to flow rates, acid and metal concentrations play a role in osmosis. The operator must be aware of the potential for osmosis to occur and react accordingly. For example, a mass balance on the process may indicate that the system is recovering 95% of the acid feed. However, due to osmosis, the acid concentration in the diffusate will not be 95% of the original feed acid concentration.

2.2 Performance Evaluation

Diffusion dialysis system performance is determined through calculations using recorded flow rates and concentrations of the feed acid, diffusate, and dialysate streams. The two main performance indicators are percent acid recovery and percent metal rejection in the diffusate. Percent acid recovery is determined using mathematical equation 2.2.1. Percent metal rejection is determined using mathematical equation 2.2.2.

$$\% \text{ Acid Recovery} = 100 \times (F_{diff} \times Acid_{diff}) / [(F_{diff} \times Acid_{diff}) + (F_{dial} \times Acid_{dial})] \quad \text{(Eq. 2.2.1)}$$

Where,

F_{diff} = Diffusate flow rate
$Acid_{diff}$ = Diffusate acid concentration
F_{dial} = Dialysate flow rate
$Acid_{dial}$ = Dialysate acid concentration

$$\% \text{ Iron Rejection} = 100 \times (F_{dial} \times Met_{dial}) / [(F_{diff} \times Met_{diff}) + (F_{dial} \times Met_{dial})] \quad \text{(Eq. 2.2.2)}$$

Where,

F_{dial} = Dialysate flow rate
Met_{diff} = Dialysate metal concentration
F_{diff} = Diffusate flow rate
Met_{dial} = Diffusate metal concentration

3.0 ACID SORPTION THEORY

Acid sorption is a chemical technology designed to separate dissolved metals and complexed acid from free acid. Ion exchange resin is utilized to adsorb free acid while allowing complexed acid and dissolved metals to pass. The main steps in purifying metal contaminated mineral acid with this system are a

loading step in which the free acid is adsorbed onto the resin, and a regeneration step in which water is passed over the loaded resin to pull off the free acid.

The process sequence for the equipment used for this demonstration/validation involves four steps. The four steps are:

- Step 1 - Volume V_b of feed acid is pumped from the feed acid reservoir through the resin column, displacing the water resident on the column from the previous cycle. The free acid is adsorbed by the resin as it passes through the column and the displaced water returns to the water reservoir.

- Step 2 - Volume V_a of feed acid is pumped into the column displacing volume V_b which contains the metal salts and any residual acid. This step produces the by-product.

- Step 3 - Volume V_c of water flows countercurrently into the column and displaces unprocessed acid back to the acid reservoir.

- Step 4 - Volume V_d of water, also flowing countercurrently, displaces the acid rich product to the recovered acid storage tank. This cycle of four steps is repeated in approximately five minute intervals.

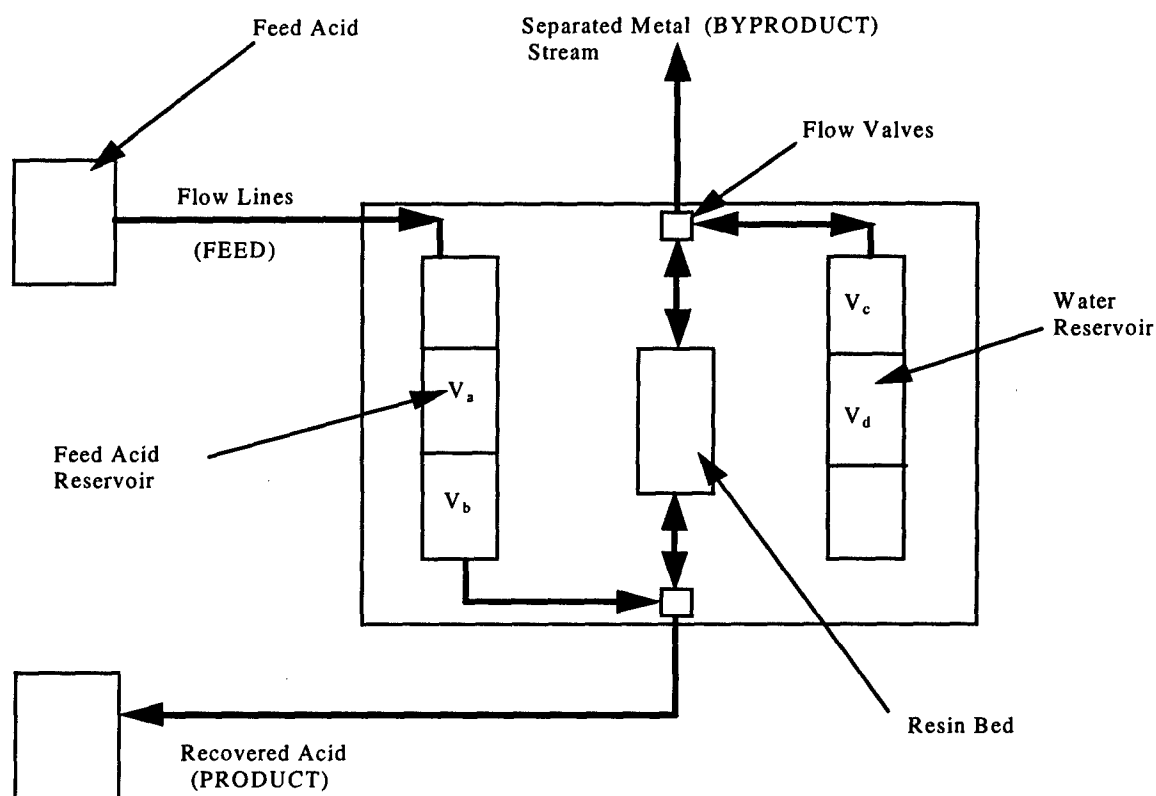Figure 2 schematically illustrates the system used for this work.

Figure 2. Schematic of Acid Sorption System

3.1 Process Considerations

The resin column used for testing was 2 inches in diameter and 12 inches long. Column diameter will be increased for larger scale applications requiring higher resin volume. The resin used in the acid sorption system is proprietary.

The volumes and flow rates for each process step must be set according to the manufacturers instructions. Varying the flow rates of acid feed and water feed streams affects the recovery and removal efficiencies to a small degree.

Time to achieve equilibrium for this system is approximately one half hour. After initial start up the recovered acid and by-product streams are sampled and analyzed for free acid content. Equilibrium is considered to be reached when the variation of acid concentration varies by only five to ten percent between sequential cycles. The system was then allowed to run for four or five cycles to collect representative samples for analysis and comparison.

3.2 Performance Evaluation

Acid sorption system performance is determined by performing calculations using the data from each process cycle. The two main performance indicators are acid recovery efficiency and metal removal efficiency. Acid recovery efficiency is determined using mathematical equation 3.2.1. Metal removal efficiency is determined using mathematical equation 3.2.2.

$$A_{eff} (\%) = [(A_{prod} \times Prod_{vol}) / (A_{feed} \times Feed_{vol})] \times 100 \qquad \text{(Eq. 3.2.1)}$$

Where,

A_{eff} = Acid recovery efficiency
A_{prod} = Product stream acid concentration
$Prod_{vol}$ = Product volume collected during cycle
A_{feed} = Feed solution acid concentration
$Feed_{vol}$ = Feed solution volume processed during cycle

$$Met_{eff} (\%) = [(Met_{prod} \times Prod_{vol}) / (Met_{feed} \times Feed_{vol})] \times 100 \qquad \text{(Eq. 3.2.1)}$$

Where,

Met_{eff} = Metal recovery efficiency
Met_{prod} = Product stream metal concentration
$Prod_{vol}$ = Product volume collected during cycle
Met_{feed} = Feed solution metal concentration
$Feed_{vol}$ = Feed solution volume processed during cycle

4.0 EXPERIMENTAL APPROACH

All experimentation and analysis was performed by Concurrent Technologies Corporation (*CTC*). The purpose of this experiment was to objectively evaluate and compare the performance and applicability of diffusion dialysis and acid sorption for purifying mineral acids.

Bench scale equipment was used to perform all testing. The time required to reach equilibrium for the diffusion dialysis system and the overall time constraints for performing the tests, allowed for only two trials for each technology to be performed. Solutions believed to be representative of those commonly used in industry were selected as the test solutions. The test solutions consisted of two hydrochloric acid (HCl) solutions at different acid concentrations contaminated with different concentrations of iron (Fe). They were to represent a typical HCl steel cleaning bath and an HCl steel activation bath. Synthetic solutions were formulated on-site to represent these typical baths. Table 1 illustrates the concentrations used for testing.

TABLE 1. TEST SOLUTION CONCENTRATIONS

Trail #	Solution	Diffusion Dialysis		Acid Sorption	
		HCl (g/l)	Fe (g/l)	HCl (g/l)	Fe (g/l)
1	Cleaning	45.5	37.4	45.3	38.1
2	Activating	131	66.1	136	68.4

4.1 Diffusion Dialysis Set-up

Each trial for the diffusion dialysis system was run continuously for approximately 104 hours. Flow rates were selected such that the dialysate flow was faster than the diffusate flow. The ratio of dialysate to diffusate flow was kept in the range of 1.1 to 1.2. The flow rates were maintained constant throughout the trial. This was done in attempt to achieve higher acid recovery while possibly sacrificing metal rejection performance. Again, due to time constraints, it should be noted that the flow rates were not optimized. Measurement of flow was performed using a calibrated stopwatch and a graduated cylinder. To assure reasonable accuracy in measurement, the flow rate data used was an average of three measurements taken sequentially.

For material balance purposes, the volume of feed acid and deionized water fed to the system was measured. This was done by measuring the liquid height in the head tank and calculating the volume using the known length and width dimensions.

Grab samples of diffusate and dialysate were taken twice daily for analysis. Flow rates were also measured at this time. The feed acid and deionized water head tanks were sampled only once a day. These samples were analyzed for free acid and total iron content using titration standard ASTM E 224, and Inductively Coupled Plasma (ICP) standard EPA 200.7, respectively. To ensure the integrity of the data, all samples were analyzed using the appropriate QA/QC procedures.

4.2 Acid Sorption Set-up

The bench scale acid sorption equipment was run at the manufacturers recommended flow rates. These process settings were stated as being the optimum conditions to run for the given feed solutions. Flow rates were obtained by measuring product and by-product volumes and dividing them by the cycle time, which was measured using a calibrated stopwatch.

Grab samples of the recovered acid and by product stream were taken after start-up to note when equilibrium was reached. Once equilibrium was achieved, four samples from sequential cycles were collected for laboratory analysis. Feed, recovered acid, and by-product were analyzed for free acid and total iron content using titration standard ASTM E 224, and ICP standard EPA 200.7, respectively. All necessary QA/QC procedures were followed to ensure data integrity.

5.0 RESULTS

The raw data was collected and reduced using the equations described above. The results were then presented in graphical formats to clearly convey and compare the performance of the two systems. Performance results for each technology are compiled and given below.

5.1 Diffusion Dialysis Results

The percent acid recovery and percent iron rejection results varied slightly throughout the time of each trial. These minor variations were judged to be insignificant (+/- 0.5 - 1.5% variation). Trial 1 had an average acid recovery of 97% and an average iron rejection of 89%. Trial 2 had average acid recovery of 98% and average iron rejection of 83%. Figure 5.1.1 illustrates the trend of percent acid recovery for the entire time of each trial. Figure 5.1.2 illustrates the trend of percent iron rejection for the entire time of each trial.
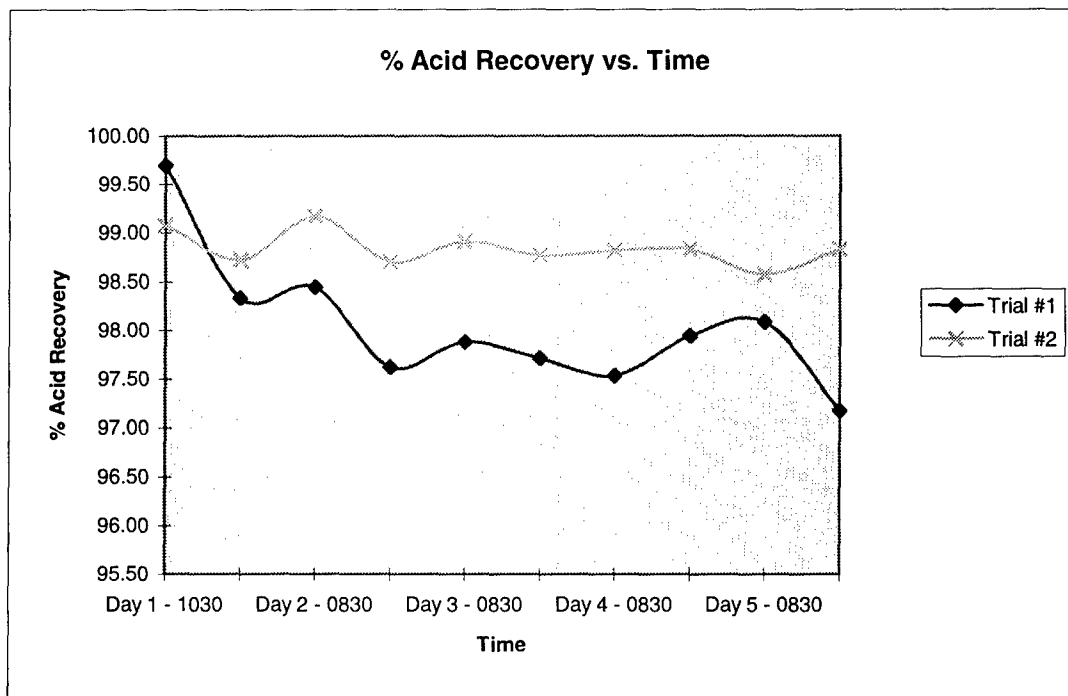

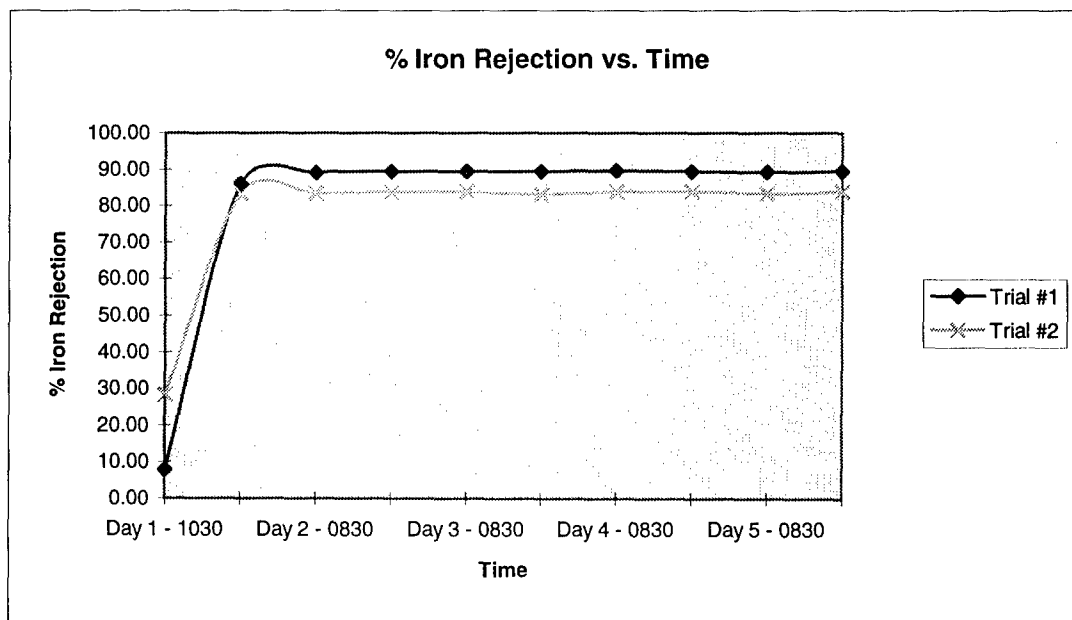Figure 5.1.1. Percent acid recovery for each trial

Figure 5.1.2. Percent iron rejection for each trial

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After performing the overall material balance for each trial it is evident that osmosis was substantially diluting the feed acid and causing the concentration of acid in the diffusate to be significantly lower than that of the feed. Based on calculated percent acid recoveries for trials one and two, the concentrations of acid in the diffusate were expected to be approximately 44 g/l and 128 g/l, respectively. Actual concentrations of the diffusate streams were approximately half of the acid feed stream. Table 2 presents these results and illustrates the differences in acid concentration between the feed and diffusate. Again, it is important to note that flow rates were note optimized in these tests. Varying flow rates will minimize the dilution of the feed acid caused by osmosis. This can effect can be manipulated advantageously depending on the desired results in actual operation (i.e. recovered acid purity vs. metal rejection).

TABLE 2. DIFFUSION DIALYSIS FEED AND DIFFUSATE COMPARISON

Trial #	HCl in Feed (g/l)	HCl in Diffusate (g/l)	% Dilution
1	45.5	26.9	~41
2	131	73.9	~44

5.2 Acid Sorption Results

Results for the acid sorption trials presented here are the mathematical average of four samples taken from sequential cycles after reaching equilibrium. The average acid recovery and iron removal efficiencies are given in Table 3.

TABLE 3. AVERAGE ACID SORPTION EFFICIENCIES

Trial #	HCl Recovery Efficiency (%)	Fe Removal Efficiency (%)
1	97.7	47.0
2	94.3	41.6

Observing the acid concentration in the feed acid and the recovered acid product indicates that the product has a higher acid concentration than the feed. This occurs because the quantity of water used to recover the acid was less than the quantity of acid fed to the column. Therefore, the concentration increase is not an indication that acid is produced, but simply that the same quantity of acid is present in a smaller volume of liquid. The comparison of feed acid to recovered acid product is given in Table 4. Of special interest is the fact that although the recovered acid was more concentrated than that of the diffusion dialysis, the recovered acid was less pure than the diffusion dialysis recovered acid. A comparison of iron in the feed and product streams for both technologies is given in Table 5.

TABLE 4. ACID SORPTION FEED AND PRODUCT COMPARISON

Trial #	HCl in Feed (g/l)	HCl in Diffusate (g/l)	% Concentration
1	45.3	47.2	~104
2	136	145	~107

TABLE 5. PRODUCT STREAM PURITY COMPARISON

Trail #	Diffusion Dialysis		Acid Sorption	
	Fe in feed (g/l)	Fe in diffusate (g/l)	Fe in feed (g/l)	Fe in product (g/l)
1	37.4	2.2	38.1	21.7
2	66.1	5.9	68.4	42.6

CONCLUSIONS

It should be noted that the results presented here are only based on two trials. Also, due to time constraints, the diffusion dialysis system was not operated at optimized process settings. Therefore, the performance of the diffusion dialysis system may have considerable room for improvement if optimized settings were achieved.

Conclusions for diffusion dialysis are:
- the diffusion dialysis system has a higher HCl recovery efficiency per gram of acid fed to it, but because of the degree of osmosis occurring within the membrane stack in this instance, the diffusate acid concentration is approximately only 55 - 60% of the feed acid concentration,
- the diffusion dialysis system achieves greater percent rejection of the contaminant metal in the feed; approximately 52% higher than acid sorption in this case (osmosis acts to increase metal rejection)
- fresh make up acid will be required when processing a work tank with a diffusion dialysis system (quantity will be dependent on system performance and the ability to minimize osmosis),

Conclusions for acid sorption are:
- the acid sorption system has a lower HCl recovery efficiency per gram of acid fed to it, but because of how it was operated, the recovered acid product is actually more concentrated than the feed,
- the acid sorption system will eliminate the need for make up acid into the working tank (the recovered acid product will actually need diluted prior to re-introduction to the working tank),
- average metal removal efficiency range from the feed to product stream is 38 - 44%

These technologies may be operated in batch or continuous mode. Diffusion dialysis is more suited for continuous mode, due to the time required to reach equilibrium. Acid sorption has more flexibility to operate efficiently in either mode. Choosing a technology and mode of operation will be dependent on purity requirements of the bath, the bath volume to be processed, and the required flow rate. Operating costs for each system will be minimal due to their simplicity. Equipment costs and product purity requirements will govern technology selection. These factors will vary from one application to another. Applications that require high bath purity and a low feed processing rate may be best suited for diffusion dialysis. Conversely, applications requiring higher feed processing rates, and less stringent bath purity may be more conducive to acid sorption. Correct technology selection must be based on the actual application and will vary based on the mineral acid and metal contaminant concentrations.

Overall, both technologies provide viable at-source opportunities for recovering acid and minimizing waste handling costs, while maintaining higher quality baths and increased productivity.